PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 07 August 2000 (07.08.00)	
International application No. PCT/GB99/03997	**Applicant's or agent's file reference** 9.67446/001
International filing date (day/month/year) 30 November 1999 (30.11.99)	**Priority date** (day/month/year) 30 November 1998 (30.11.98)
Applicant WILLIAMS, Gareth et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

23 June 2000 (23.06.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Pascal Piriou

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
9.67446/001		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/GB 99/03997	30/11/1999	30/11/1998
Applicant		
HICKSON INTERNATIONAL PLC et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rul 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from th date of mailing of this international search report, submit comments to this Authority.

6. The figure of th **drawings** to be published with the abstract is Figure No. _____

   [ ] as suggested by the applicant.

   [ ] because th applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [X] None of the figures.

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INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 99/03997

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B27K3/50 A01N43/88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N B27K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 06043 A (UNIROYAL CHEM CO INC ;UNIROYAL CHEMICAL LTD (CA)) 2 March 1995 (1995-03-02) page 12, line 1-17; claim 4 ---	1
A	EP 0 104 940 A (UNIROYAL INC ;UNIROYAL LTD (CA)) 4 April 1984 (1984-04-04) ---	
A	WO 95 05739 A (JANSSEN PHARMACEUTICA NV ;GESTEL JOZEF FRANS ELISABETHA (BE)) 2 March 1995 (1995-03-02) ------	

☐ Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 February 2000	09/03/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Dalkafouki, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. onal Application No
PCT/GB 99/03997

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9506043 A	02-03-1995	AT 154017 T	15-06-1997
		AU 688371 B	12-03-1998
		AU 7640194 A	21-03-1995
		BR 9407561 A	31-12-1996
		CA 2169654 A	02-03-1995
		CN 1133039 A	09-10-1996
		CZ 9600560 A	17-07-1996
		DE 69403667 D	10-07-1997
		DE 69403667 T	16-10-1997
		DK 715625 T	15-12-1997
		EP 0715625 A	12-06-1996
		ES 2102878 T	01-08-1997
		FI 960829 A	19-04-1996
		GR 3024590 T	31-12-1997
		HU 74480 A,B	28-01-1997
		JP 2761441 B	04-06-1998
		JP 8509986 T	22-10-1996
		NO 960696 A	21-02-1996
		NZ 273187 A	27-05-1998
		PL 313136 A	10-06-1996
		US 5777110 A	07-07-1998
		ZA 9406450 A	30-06-1995
EP 0104940 A	04-04-1984	AU 544881 B	20-06-1985
		AU 1961883 A	05-04-1984
		BR 8305330 A	08-05-1984
		CA 1273921 A	11-09-1990
		DD 215781 A	21-11-1984
		ES 525994 A	16-09-1985
		GB 2127817 A,B	18-04-1984
		GR 78990 A	02-10-1984
		JP 59080670 A	10-05-1984
		US 4569690 A	11-02-1986
		US 4675044 A	23-06-1987
WO 9505739 A	02-03-1995	AP 568 A	25-11-1996
		AT 163836 T	15-03-1998
		AU 680294 B	24-07-1997
		AU 7654494 A	21-03-1995
		BR 9407567 A	31-12-1996
		CA 2168357 A	02-03-1995
		CN 1129894 A	28-08-1996
		CZ 9600463 A	15-05-1996
		DE 69408998 D	16-04-1998
		DE 69408998 T	25-06-1998
		EP 0715495 A	12-06-1996
		ES 2113674 T	01-05-1998
		FI 960848 A	23-02-1996
		GR 3026333 T	30-06-1998
		HK 1006054 A	05-02-1999
		HU 74291 A,B	28-11-1996
		JP 9501688 T	18-02-1997
		NO 960728 A	23-02-1996
		NZ 273306 A	27-07-1997
		PL 313133 A	10-06-1996
		SG 66277 A	20-07-1999
		SK 23296 A	05-06-1996
		US 5712275 A	27-01-1998

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/03997

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9505739 A		US 5922113 A	13-07-1999
		ZA 9406449 A	26-02-1996

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
9.67446/001		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB99/03997	30/11/1999	30/11/1998
International Patent Classification (IPC) or national classification and IPC B27K3/50		
Applicant HICKSON INTERNATIONAL PLC et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

I	☒	Basis of the report
II	☐	Priority
III	☐	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	☒	Lack of unity of invention
V	☒	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
VI	☐	Certain documents cited
VII	☒	Certain defects in the international application
VIII	☒	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
23/06/2000	20.02.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Nissen, V Telephone No. +49 89 2399 8619

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/03997

I. Basis of the rep rt

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:
Description, pages:

1-24 as originally filed

Claims, No.:

1-13 as originally filed

Drawings, sheets:

1-5 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

   ☐ restricted the claims.

   ☐ paid additional fees.

   ☐ paid additional fees under protest.

   ☐ neither restricted nor paid additional fees.

2. ☒ This Authority found that the requirement of unity of invention is not complied and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

   ☐ complied with.

   ☒ not complied with for the following reasons:
   see separate sheet

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

   ☒ all parts.

   ☐ the parts relating to claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1, 3-7, 9-12
Inventive step (IS)	Yes:	Claims
	No:	Claims 2, 8, 13

Industrial applicability (IA) Yes: Claims 1-13
No: Claims

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item VIII **Certain observations on the international application**

1. The subject matter of present claim 1 is unclear (Art. 6 PCT) as it appears to lack essential features necessary to define the invention (R. 6.3(a) PCT). The composition is partly functionally defined by its desired "synergistic" properties rather than by the structural, technical features capable of providing said properties (R. 6.3(a) PCT). The claimed subject matter thus has the character of a mere desideratum (Art. 6 PCT, Guidelines III-4.7). See also blow section V, item 2.1.

1.1 The composition according to claim 1 makes reference to a "synergistic" effect, however, without defining in respect of what the synergism is exhibited and how it is to be measured. Accordingly the subject matter of claim 1 per se is unclear (Art. 6 PCT).

1.2 From reading claim 1 alone it is not clear whether both a quaternary ammonium compound and a triazole compound must be present (Art. 6 PCT).

1.3 Also the nature of the triazole compound is not clear (Art. 6 PCT). In the description on page 7, line 22 it is mentioned that the triazole compound only preferably contains the triazole group.

2. The subject matter of claim 3 is not clear (Art. 6 PCT) as it is not clear which of the listed substituents belong to the group defining R (a) per se and which belong to the group of 1-3 substituents of the optional phenyl (R= substituted phenyl).

3. The subject matter of claims 9 and 12 is unclear (Art. 6 PCT) because the nature of "other material" has not been defined.

3.1 It is also not clear (Art. 6 PCT) what would be considered as falling within the definition of being "affected by" or "at risk of being affected" as stated in claims 10 and 11.

3.2 Moreover, it is not clear which technical problem is solved by the subject matter of claims 9 and 12 if the substrate is not susceptible to degradation by fungi or other micro organisms (R.5.1(a)(iii) and 6.3(a).

Re Item V **Reasoned statement under Rule 66.2(a)(ii) with regard to nov lty, inventive step or industrial applicability; citations and explanati ns supporting such statement**

Reference is made to the following documents:

D1: WO 95 06043 A (UNIROYAL CHEM CO INC ;UNIROYAL CHEMICAL LTD (CA)) 2 March 1995 (1995-03-02)
D2: EP-A-0 104 940 (UNIROYAL INC ;UNIROYAL LTD (CA)) 4 April 1984 (1984- 04-04)
D3: WO 95 05739 A (JANSSEN PHARMACEUTICA NV ;GESTEL JOZEF FRANS ELISABETHA (BE)) 2 March 1995 (1995-03-02)

1. The use of oxathiazines in compositions for preserving wood is known from D1 [the abstract]. The oxathiazines according to D1 appear to be essentially the same as the ones defined in present claims 3-5 [page 3-6]. Moreover, it is known to use these oxathiazines in combination with other fungicides such as various triazoles (e.g. as falling within the definitions given in claims 6 and 7) in order to optimize overall effectiveness of the composition [page 12, lines 2-17].

1.1 In essence D1 discloses one list of generally known agents to be combined with the (single) known oxathiazine in order to optimize the fungicidal effectiveness thereof. The subject matter of present claim 1 is therefore not considered to be a "selection invention" from the disclosure of D1. Moreover, any beneficial technical effect of the combinations disclosed in D1 will be inherent to said compositions and it is clear from the present description that the relative amounts of the additive agents to the amount of oxathiazine of D1 lies within the ranges considered as

"synergistic" by the applicant. Accordingly the subject matter of claims 1, 3-7 and 9-12 is considered to lack novelty over D1 (Art. 33(2) PCT).

1.2 In so far Ascomycotina and/or Deuteromycotina are commonly known as undesired fungi in wood, it is not considered as involving an inventive step to use a composition comprising oxathiazine and an "enhancer" in terms of a triazole for preserving the wood against said fungi. Moreover, it would merely constitute an inherent effect by using the compositions of D1 for the intended purpose. Accordingly it is considered that the subject matter of present claim 13 lacks an inventive step over D1 if not implicitly known therefrom (Art. 33(2) or (3) PCT).

2. Regarding compositions comprising oxathiazine and a quaternary ammonium compound it is noted that none of the cited prior art documents discloses such composition explicitly. However, D1-D3 disclose the use of oxathiazine in compositions which also comprise surfactants, wetting agents and/or emulsifiers [D1 page 8, lines 25-27; D3 page 7, lines 4-22 and page 9; D2 page 4, line 34]. Quaternary ammonium compounds are well known representatives of compounds falling within the said classes. Moreover such compounds are generally known to have biocidal properties and could in this respect also be considered as suitable additives [D1 page 9, lines 2-3; page 12, lines 17-21].

2.1 In this respect it is noted that only the quaternary ammonium compound designated "Bardap 26" has been demonstrated to have a particular fungicidal effect. It is, however, considered unlikely that <u>any</u> quaternary ammonium (or <u>any</u> triazole compound for that matter) is capable of providing a "synergistic" effect with <u>any</u> oxathiazine merely by choosing appropriate amounts of the components as otherwise is the only requirements according to claim 1 (Art. 6, 33(3) and R.6.3a PCT).

2.2 In so far there is no evidence making it plausible that a surprising effect is present for all compounds falling within the definitions of a composition <u>per se</u> given in claims 2 and 8 they would appear to constitute obvious

combinations of per se known compounds (Art. 33(3) PCT).

3. Industrial applicability is self-evident for the subject matter of all claims (Art. 33(4) PCT).

Re Item IV **Lack of unity**

1. In view of the subject matter of claim 1 being not novel, a common novel and inventive link between using triazoles and/or ammonium compounds in connection with oxathiazines does not exist (Art. 3.4(iii) and R. 13 PCT).

Re Item VII **Certain defects in the international application**

1. The independent claims are not in the two-part form in accordance with Rule 6.3(b) PCT, which in the present case would be appropriate, with those features known in combination from the prior art (D1) being placed in the preamble (Rule 6.3(b)(i) PCT) and with the remaining features being included in the characterising part (Rule 6.3(b)(ii) PCT).

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : B27K 3/50, A01N 43/88 — A1

(11) International Publication Number: WO 00/32371

(43) International Publication Date: 8 June 2000 (08.06.00)

(21) International Application Number: PCT/GB99/03997

(22) International Filing Date: 30 November 1999 (30.11.99)

(30) Priority Data:
9826245.4 30 November 1998 (30.11.98) GB

(71) Applicants *(for all designated States except US)*: HICKSON INTERNATIONAL PLC [GB/GB]; Wheldon Road, Castleford, West Yorkshire WF10 2JT (GB). JANSSEN PHARMACEUTICA N.V. [BE/BE]; Turnhoutseweg 30, B–2340 Beerse (BE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: WILLIAMS, Gareth [GB/GB]; Hickson Timber Products Ltd., Wheldon Road, Castleford, West Yorkshire WF10 2JT (GB). BACON, Michael [GB/GB]; Hickson Timber Products Ltd., Wheldon Road, Castleford, West Yorkshire WF10 2JT (GB).

(74) Agents: GARDNER, Rebecca et al.; Frank B. Dehn & Co., 179 Queen Victoria Street, London EC4V 4EL (GB).

(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: WOOD PRESERVATIVE FORMULATIONS

(57) Abstract

The invention provides a preservative composition comprising, in synergistic proportions, an oxathiazine compound plus one or more of a quaternary ammonium compound and a triazole compound as well as methods of treating wood and other material with said compositions.

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CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

Wood Preservative Formulations

This invention relates to preservatives for wood and other materials, in particular to preservative formulations which contain an oxathiazine.

The use of oxathiazines in wood preservation is known (WO 95/06043 of Uniroyal Chemical Company, Inc.). These oxathiazines are most active against the soft rot fungi *Ascomycotina* and *Deuteromycotina*. These organisms are often responsible for significant degradation of wood in practice (Eaton and Hale (1993)).

As with most individual active ingredients, oxathiazines by themselves do not provide protection against all fungi, bacteria, and other microorganisms which it is desirous to protect wood or other materials against. Therefore, WO 95/06043 discusses the possibility of enhancing the spectrum of activity by addition of other active ingredients, binding agents, co-solvents etc.

Organic wood preservative formulations such as those containing oxathiazines are expensive to formulate and manufacture and improvements in their performance against fungi, particularly *Ascomycotina* and *Deuteromycotina*, would therefore be of benefit to the wood preservative industry.

Surprisingly, it has been found that by addition of certain other organic biocides, the efficacy of the oxathiazine-based formulations is significantly increased. In the case of some oxathiazines which have on their own poor efficacy, the addition of other organic biocides results in formulations having excellent efficacy, particularly against *Ascomycotina* and *Deuteromycotina*.

We have found that for an increase in activity of oxathiazine containing formulations against *Ascomycotina*

and *Deuteromycotina*, it is not a requirement that the additional organic biocides themselves have good activity against these fungi. A synergistic relationship has been observed, whereby oxathiazines and other organic biocides having individually moderate or poor efficacy against *Ascomycotina* and *Deuteromycotina*, when present together in a formulation provide a highly effective wood preservative agent.

The additional organic biocide is a quaternary ammonium compound or a triazole compound.

According to one aspect therefore, the present invention provides a preservative composition comprising, in synergistic proportions, an oxathiazine compound plus one or more of a quaternary ammonium compound and a triazole compound.

Particularly preferred compositions according to the invention comprise, in synergistic proportions, an oxathiazine compound, a quaternary ammonium compound and a triazole compound.

In a further aspect, the invention provides a method of preserving wood or other material which comprises applying to the wood or other material a composition comprising an oxathiazine compound plus one or more of a quaternary ammonium compound and a triazole compound in synergistic proportions.

The other materials besides wood which can benefit from treatment with the formulations of the invention include cellulosic material such as cotton. Also, leather, textile materials and even synthetic fibres, hessian, rope and cordage as well as composite wood materials. For convenience, the invention will be described with reference to the treatment of wood but it will be appreciated that other materials may be treated analogously.

The application of these compositions may be by dipping, spraying, brushing or other surface coating means or by high pressure or double vacuum impregnation

into the body of the wood or other material, all being techniques well known to the man skilled in the art. Impregnation under pressure is particularly advantageous when the substrate is wood or a wood composite material which is made to become wet during its life, for example, wood for window frames, timber used above ground in exposed environments such as decking and timber used in ground contact or fresh water or salt water environments.

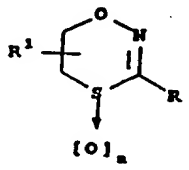
According to a further aspect of the invention there is provided the use of a quaternary ammonium compound or a triazole to enhance the activity of an oxathiazine against *Ascomycotina* and *Deuteromycotina*.

Substrates made of wood or other material which have been treated with a composition or by a method according to the invention as described herein, comprise further aspects of the present invention.

Certain compositions according to the invention are particularly advantageous from an environmental point of view, as they provide excellent heavy metal free compositions for protecting wood when it is in contact with soil, as the oxathiazine additionally protects the wood against soil bacteria such as Alcaligenes, Bacillus, Clostridium, Pseudomonas, etc.

Preferably, the compositions are applied to timber components before they are used in construction but they can also be used remedially as a curative action in preventing continued wood degradation or defacement.

Oxathiazine compounds for use in the present invention include, for example, oxathiazine compounds of formula (I)



(I)

wherein n is 0, 1 or 2; R^1 is hydrogen, C_1-C_4 linear or branched alkyl, or benzyl; and

R is:

(a) phenyl; naphthyl; phenyl substituted with 1 to 3 of the following substituents:

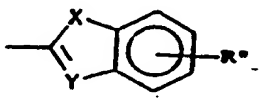
hydroxyl, halo, C_1-C_{12} alkyl, C_5-C_6 cycloalkyl, trihalomethyl, phenyl, C_1-C_5 alkoxy, C_1-C_5 alkylthio, tetrahydropyranyloxy, phenoxy, (C_1-C_4 alkyl)carbonyl, phenylcarbonyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, carboxy or its alkali metal salt, (C_1-C_4 alkoxy)carbonyl, (C_1-C_4 alkyl)aminocarbonyl, phenylaminocarbonyl, tolylaminocarbonyl, morpholinocarbonyl, amino, nitro, cyano, dioxolanyl, or (C_1-C_4 alkoxy)iminomethyl;

pyridinyl; thienyl, preferably when n is not 2; furanyl; or thienyl or furanyl substituted with 1 to 3 of the following groups:

alkyl, alkoxy, alkylthio, alkoxycarbonyl, halogen, trihalomethyl, cyano, acetyl, benzoyl, nitro, formyl, alkoxyaminomethyl, phenyl, or phenylaminocarbonyl, wherein the alkyl or alkoxy moiety is C_1-C_4, linear or branched;

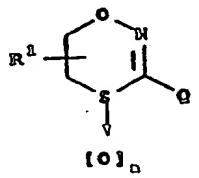
or

(b)



wherein X is oxygen or sulfur; Y is nitrogen, -CH-, or -C(C_1-C_4 alkoxy)-; and R" is hydrogen or C_1-C_4 alkyl.

Preferably the oxathiazine compound has the formula (II)



(II)

wherein n is 0, 1 or 2, R^1 is hydrogen, C_1-C_4 linear or branched alkyl, or benzyl; and

Q is:

(a)

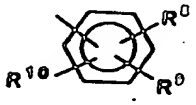
wherein R^2, R^3 and R^4 are, individually, hydrogen, alkyl, alkoxy, alkylthio, alkoxycarbonyl, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, alkoxyaminomethyl, phenyl, or phenylaminocarbonyl, wherein the alkyl or alkoxy moieties are all C_1-C_4, linear or branched, with the proviso that at least one of R^2, R^3 or R^4 must be other than hydrogen;

(b)

wherein R^5, R^6 and R^7 are, individually, hydrogen, C_1-C_4 alkoxy, C_1-C_4 alkylthio, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, phenyl, or

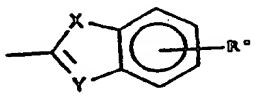
phenylaminocarbonyl, with the proviso that at least one of R^5, R^6 or R^7 must be other than hydrogen;

(c)



wherein R^8, R^9 and R^{10} are, individually, hydroxyl, halo, C_1-C_{12} alkyl, C_5-C_6 cycloalkyl, trihalomethyl, phenyl, C_1-C_5 alkoxy, C_1-C_5 alkylthio, tetrahydropyranyloxy, phenoxy, (C_1-C_4 alkyl)carbonyl, phenylcarbonyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, carboxy or its alkali metal salt, (C_1-C_4 alkoxy)carbonyl, (C_1-C_4 alkyl)aminocarbonyl, phenylaminocarbonyl, tolylaminocarbonyl, morpholinocarbonyl, amino, nitro, cyano, dioxolanyl, or (C_1-C_4 alkoxy)iminomethyl; or

(d)



wherein X is oxygen or sulfur; Y is nitrogen, -CH-, or -C(C_1-C_4 alkoxy)-; and R" is hydrogen or C_1-C_4 alkyl.

More preferably, the oxathiazine is a compound of formula II wherein

R^1 is hydrogen or C_1-C_4 alkyl; n is 1 or 2;

R^2, R^3 and R^4 are, individually, hydrogen, C_1-C_4 alkyl, halo, (C_1-C_4 alkoxy)-carbonyl, or cyano, with the proviso that at least one of R^2, R^3 and R^4 must be other than hydrogen;

R^5, R^6 and R^7 are, individually, hydrogen, halo or cyano, with the proviso that at least one of R^5, R^6 and R^7 must be other than hydrogen;

R^8, R^9 and R^{10} are C_1-C_4 alkyl, C_1-C_4 alkoxy, nitro, halo, trihalomethyl, or (C_1-C_4 alkoxy)-carbonyl; X is

sulfur; and R" is hydrogen.

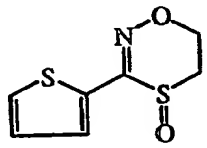
More preferred are those compounds of formula (II) wherein R^1 is hydrogen; n is 1 or 2;

R^2, R^3 and R^4 are, individually, hydrogen, methyl, ethyl, bromo, chloro, ethyl carboxylate, or cyano, with the proviso that at least one of R^2, R^3 and R^4 must be other than hydrogen;

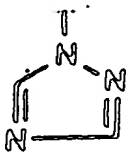
R^5, R^6 and R^7 are, individually, hydrogen, bromo, chloro, or cyano, with the proviso that at least one of R^5, R^6 and R^7 must be other than hydrogen;

R^8, R^9 and R^{10} are methyl, ethyl, nitro, fluoro, chloro, or trifluoromethyl.

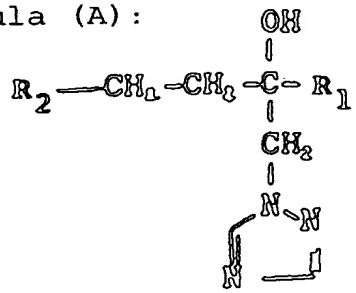
The most preferred oxathiazine compounds for use in the compositions and methods of the present invention are 3-(benzo[b]thien-2-yl)-5,6-dihydro-1,4,2-oxathiazine 4-oxide, hereinafter referred to as bethoxazin and 5,6-dihydro-3-(2-thienyl)-1,4,2-oxathiazine, 4-oxide,



Preferably the triazole compound contains the triazole group



Advantageously, the triazole compound is selected from compounds of formula (A):



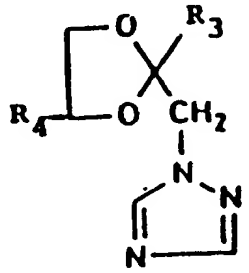
(A)

wherein R_1 represents a branched or straight chain

C_{1-5} alkyl group (e.g. t-butyl) and R_2 represents a phenyl group optionally substituted by one or more substituents selected from halogen (e.g. chlorine, fluorine or bromine) atoms or C_{1-3} alkyl (e.g. methyl), C_{1-3} alkoxy (e.g. methoxy), phenyl or nitro groups.

A particularly preferred compound of formula (A) is tebuconazole:
alpha-[2-(4-chlorophenyl)ethyl]-alpha(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol.

Alternatively, the triazole compound is advantageously selected from compounds of formula (B):



(B)

wherein R_3 is as defined for R_2 above and R_4 represents a hydrogen atom or a branched or straight chain C_{1-5} alkyl group (e.g. n-propyl).

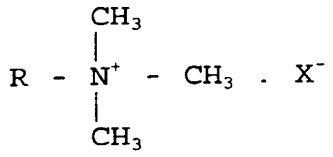
Particularly preferred triazole compounds of this type are: propiconazole (1-[[2-(2-4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole) and azaconazole (1-[[2,4-dichlorophenyl)-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole. Other triazoles which could be used include hexaconazole ((RS)-2-(2,4-dichlorophenyl)-1-(1H-1,2,4-triazol-1-yl)hexan-2-ol), difenaconazole, cyproconazole ((2RS,3RS; 2RS,3SR)-2-(4-chlorophenyl)-3-cyclopropyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol), bromuconazole (1-[4-bromo-2-(2,4-dichloro-phenyl)tetrahydrofurfuryl]-1*H*-1,2,4-triazole), epoxiconazole (1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)oxiran-2-ylmethyl]-1*H*-1,2,4-triazole), metconazole (5-[(4-chlorophenyl)-methyl]-2,2-dimethyl-1-(1*H*-1,2,4-triazol-1-ylmethyl)cyclopentanol), and triticonazole ((E)-5-(4-chloro-phenyl)methylene)-2,2-dimethyl-1-(1*H*-1,2,4-triazol-1-ylmethyl)-cyclopentanol),

fenbuconazole, flusilazole, tetraconazole and penconazole.

Compositions according to the invention may contain more than one triazole compound, for example, they may contain two or more triazoles selected from tebuconazole, propiconazole, azaconazole and cyproconazole, such as tebuconazole and propiconazole, tebuconazole and cyproconazole or a mixture of tebuconazole, propiconazole and azaconazole.

Of the quaternary ammonium compounds which may be used in the compositions and methods of the present invention, suitable compounds include:

1. Monoalkyltrimethyl ammonium salts of formula (III):

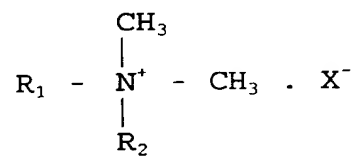


(III)

wherein R is an alkyl group having between 6 and 18 carbon atoms, preferably between 12 and 14 carbon atoms and X^- is an anion chosen to allow ready water solubility of the quaternary ammonium salt. Examples being : chloride, bromide, sulphate, acetate, propionate, lactate, citrate, methosulphate and carbonate.

Preferred examples include Cocotrimethyl ammonium chloride in which the alkyl group R consists of a mixture of predominantly C_{12} and C_{14}.

2. Dialkyl dimethyl ammonium salts of formula (IV):

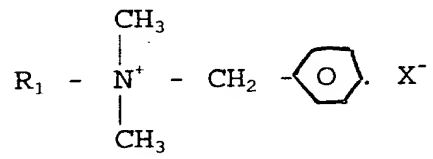


(IV)

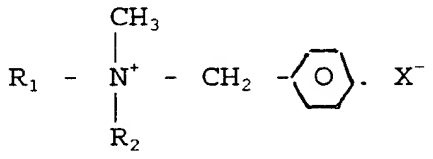
wherein R_1 and R_2 are alkyl groups which may be the same or different and which contain between 6 and 18 carbon atoms, preferably between 8 and 10 carbon atoms and X^- is an anion of the type previously described.

Preferred examples include Didecyl dimethyl ammonium chloride, dioctyl dimethyl ammonium chloride and octyl decyl dimethyl ammonium chloride either individually or as a mixture containing two or three of these.

3. Alkyl dimethyl benzyl ammonium salts and dialkyl methyl benzyl ammonium salts of formulae (V) or (VI).



(V)

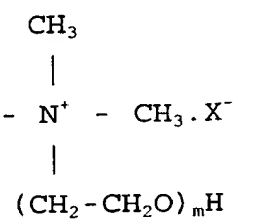


(VI)

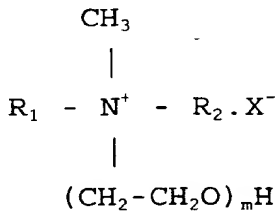
wherein R_1 and R_2 are alkyl groups which can be the same or different and which contain between 6 and 18 carbon atoms, preferably between 8 and 10 carbon atoms in a dialkyl compound and between 10 and 14 carbon atoms in a monoalkyl compound and X^- is an anion of the type previously described.

Preferred examples include Coco benzyl dimethyl ammonium chloride and dicoco benzyl methyl ammonium chloride in which the alkyl groups are predominantly C_{12} and C_{14}.

4. Alkyl and dialkyl oxyethylene methyl ammonium salts of formulai (VII) or (VIII):



(VII)



(VIII)

wherein R_1 and R_2 are alkyl groups which may be the same

or different and which contain between 6 and 18 carbon atoms, preferably between 8 and 10 carbon atoms in a dialkyl compound and between 10 and 14 carbon atoms in a monoalkyl compound, most preferably 10 carbon atoms. m is a number between 1 and 20 typically between 1 and 8, preferably between 3 and 5. X^- is an anion of the type previously described, preferably propionate or lactate.

Preferred examples include N,N-didecyl-N-methyl-poly(oxyethyl) ammonium propionate (Bardap 26) or N,N-didecyl-N-methyl-poly(oxyethyl) ammonium lactate.

5. Polymeric quaternary ammonium compounds in which active quaternary ammonium compounds are chemically grafted to a polymer backbone.

Compositions containing quaternary ammonium compounds can form micro-emulsions which are particularly useful in the treatment of timber. In addition, the presence of these compounds means that additional organic solvents may not be necessary to solubilise the triazole compound if such a compound is also present in the formulation. The inclusion of quaternary ammonium compounds may also improve penetration of the triazole compound into the timber.

The optimum weight ratio of the oxathiazine compound to the other organic biocide varies depending on the particular material to when the composition is applied, the type of organism against which protection is required and the precise conditions to which the treated material will be exposed. However, preferably, the weight ratio of oxathiazine compound to triazole and/or quaternary ammonium compound should be between 100:1 and 1:100 or 50:1 and 1:50, more preferably between 20:1 and 1:20 or 5:1 and 1:10, typically between 2:1 and 1:5. In certain preferred formulations according to the invention, the quarternary ammonium compounds will be present in excess of the oxathiazine

or triazole compound. The triazole and oxathiazine compound may be present in about equal amounts (e.g. 2:1 to 1:2 on a weight basis) and at least as much quarternary ammonium compound may be present, either as much as one of the other ingredients or as much as both of them together. For example, the ratio of quaternary ammonium compound to oxathiazine may advantageously be 1:1 to 8:1 preferably 2:1 to 5:1 on a w/w basis.

The concentration of the formulation required for preservative treatment depends on the ratio of oxathiazine to triazole or quaternary ammonium compound selected, the method of treatment employed, the timber species, the level of protection required and the nature and quantity of any other biocides present. The amounts necessary can be determined readily by one skilled in the art. In general, the amount of oxathiazine will be in the range 0.01-1.0 kgm^{-3}, the amount of triazole in the range 0.1-10.0 kgm^{-3} and the amount of quaternary ammonium compound will be in the range 0.1-10.0 kgm^{-3}; all values are expressed as the weight per unit volume of wood treated.

Conveniently, the compositions of the present invention are applied as a liquid composition, preferably by high pressure impregnation. They may also be applied as a solid implant or paste. Preferably, when applied in liquid form, this is in an aqueous solution, but one or more organic solvents or a mixture of water and an organic solvent could also be used. Suitable organic solvents include both aromatic and aliphatic hydrocarbon solvents such as white spirit, petroleum distillate, kerosene, diesel oils and naphthas. Also, benzyl alcohol, 2-phenoxy ethanol, methyl carbitol, propylene carbonate, benzyl benzoate, ethyl lactate and 2-ethyl hexyl lactate. Formulations can be prepared as concentrates intended to be diluted at the treatment facility, or the formulations can be prepared in the form of dilute treatment solutions.

The compositions according to the invention may additionally, comprise other active ingredients such as termiticides, insecticides, bacteriocides and other fungicides. Suitable additional fungicides would be apparent to one skilled in the art and will vary according to the application. In particular, additional fungicides which extend the spectrum of activity of the formulation may be chosen, such as fungicides active against bluestain fungi, white rots, brown rots, dry rots and moulds. Suitable additional fungicides include for example, dichlofluanid, acypetacs, imazalil, IPBC, isothiazolones, tolylfluanid, chlorothalonil, benzimadazoles, as well as metal compounds such as copper, Cu-oxide and Cu-HDO, also iron and zinc and salts, compounds and soaps thereof. Suitable insecticides would also be apparent to the skilled man depending upon the intended application, and include, for example, chlorpyrifos, cypermethrin, fenvalerate, fipronil, farox, teramethrin, isofenphos, permethrin, silafluofen, deltamethrin, bifenthrin, cyfluthrin and imidacloprid, and benzoylureas such as lufenuron, hexaflumuron and flufenoxuron and in particular, flurox.

The compositions according to the invention may additionally comprise other components which may act to improve the characteristics of the wood treated with these biocides. Such compounds could include water repellents based on waxes, silicones and polysiloxanes, latex, fluorocarbon, organic carboxylate/metals, paper sizing agents or amine oxides, or combinations thereof; crosslinking agents based on alkyds, acrylics, polyurethanes, formaldehydes, dimethylol, and epichlorohydrin or combinations thereof. Oils may also be used as may UV absorbers, corrosion inhibitors and defoamers.

The following non-limiting Examples further illustrate the invention.

A: Examples of formulations according to the invention for use in the preservation of wood and other materials

Those formulations which do not contain water are preferably made by weighing together all the components and blending to produce clear homogenous systems. Heating to not above 50°C may be necessary to ensure rapid dissolution of the solid active components in the solvents. Alternative methods of manufacture are possible such as solubilising the active components in water with surfactants.

Oil in water emulsions or micro-emulsions of these formulations can be prepared by adding the concentrates prepared as above to water at room temperature with good agitation to ensure proper dispersion. Emulsions containing any desired level of active component can be prepared in this way.

Those formulations containing water are formed into concentrated emulsions by taking firstly the non water containing components and blending them as for the anhydrous formulations. The required water is then added to the other components after the temperature has been allowed to return to ambient with efficient stirring to produce the concentrated emulsion. These emulsions can later be diluted to the required strength simply by adding to more water with mixing to produce diluted emulsions.

In the following Examples, Bardap 26 refers to N,N-didecyl-N-methyl-poly(oxyethyl) ammonium propionate. In all cases, the Bardap 26 preparation contains 70% of active ingredient.

Example 1

BARDAP 26/BETHOXAZIN/CYPROCONAZOLE 10:2:1

	% w/w
Bardap 26	14.29
Bethoxazin	2.00
Cyproconazole	1.00
Methyl diethoxol	66.71
Nonylphenol 12EO	16.00

Example 2

BETHOXAZIN/CYPROCONAZOLE 2:1

	% w/w
Bethoxazin	1.334
Cyproconazole	0.666
Methyl diethoxol	18.000
Dowanol PnB	10.000
Mineral oil	60.000
Tridecanol 10EO	10.000

Example 3

BARDAP 26/BETHOXAZIN/TEBUCONAZOLE/PROPICONAZOLE 10:2:0.5:0.5

	% w/w
Bardap 26	14.29
Bethoxazin	2.00
Tebuconazole	0.72
Propiconazole	0.72
Butyl glycollate	15.35
Dioctyl phthalate	46.92
Nonyl phenol 9EO	20.00

Example 4

BARDAP 26/BETHOXAZIN 10:2

	% w/w
Bardap 26	14.29
Bethoxazin	2.00
Dowanol DPM	21.79
Aromatic solvent	44.42
Castor oil 65EO	17.5

Example 5

BETHOXAZIN/TEBUCONAZOLE/PROPICONAZOLE 2:1:1

	% w/w
Bethoxazin	2.50
Tebuconazole	1.25
Propiconazole	1.25
Benzyl alcohol	14.60
Methyl octoate	58.40
Castor oil 40EO	22.00

Example 6

BETHOXAZIN/TEBUCANOZOLE 2:1

	% w/w
Bethoxazin	3.33
Tebuconazole	1.67
Butyl glycollate	23.10
Dioctyl phthalate	53.90
Nonylphenol 12EO	18.00

Example 7

BARDAP 26/BETHOXAZIN/IRON 10:2:1

	% w/w
Bardap 26	14.29

Bethoxazin	2.00
Iron naphthenate*	10.00
Oleyl alcohol 5EO	5.00
Oleyl alcohol 10EO	7.50
Dowanol PnB	15.00
Mineral oil	46.21

* Iron naphthenate in solvent containing 10.00% w/w iron metal

Example 8

BARDAP 26/BETHOXAZIN/IRON 10:2:1
Using complexed iron compound

	% w/w
Bardap 26	14.29
Bethoxazin	2.00
Iron EDTA*	11.11
Butyl glycollate	23.36
Tridecanol 15EO	12.50
Water	36.74

* Contains 9.0% w/w iron metal

Example 9

BARDAP 26/BETHOXAZIN/CYPROCONAZOLE/COPPER 10:2:1:1

	% w/w
Bardap 26	7.15
Bethoxazin	1.00
Cyproconazole	0.50
Copper gluconate*	3.57
Methyl diethoxol	14.50
Dowanol PnB	25.65
Tridecanol 13EO	15.00
Water	32.63

* Contains 14% copper metal

Example 10

BARDAP 26/BETHOXAZIN/Cyproconazole 10:2:1 plus Flurox

	% w/w
Bardap 26	14.28
Bethoxazin	2.00
Cyproconazole	1.00
Flurox	1.00
Methyl diethoxol	65.71
Nonyl phenol 12EO	16.00

Example 11

BARDAP 26/BETHOXAZIN + Farox 10:2 plus Farox

	% w/w
Bardap 26	14.28
Bethoxazin	2.00
Farox	1.50
Dowanol DPM	21.29
Aromatic solvent	43.42
Castor oil 65EO	17.51

Example 12

BETHOXAZIN/Tebuconazole 2:1 + Cypermethrin

	% w/w
Bethoxazin	3.33
Tebuconazole	1.67
Cypermethrin	2.00
Butyl glycolate	22.10
Dioctyl phthalate	52.90
Nonyl phenol 12EO	18.00

Example 13

Bardap 26/BETHOXAZIN/Iron 10:2:1 + Cyfluthrin

	% w/w
Bardap 26	14 29
Bethoxazin	2.00
Cyfluthrin	1.00
Iron EDTA*	11.11
Butyl glycolate	22.86
Tridecanol E015	12.00
Water	36.74

* contains 9% w/w iron metal.

Example 14

BARDAP 26/BETHOXAZIN/TEBUCONAZOLE/PROPICONAZOLE 10:2:0.5:0.5

	% w/w
Bardap 26	14.29
Bethoxazin	2.00
Tebuconazole	0.5
Propiconazole	0.5
Butyl glycollate	15.79
Dioctyl phthalate	46.92
Nonyl phenol 9EO	20.00

Synergistic action of mixtures formulated according to the invention

The toxic limit value for a particular biocidal compound is the concentration of the compound which is required to prevent degradation (defined as >3% mass loss) of a substrate by a target organism. Toxic limits are normally expressed as two experimentally-determined

concentrations that span the pass/fail point of the test. The toxic index is the midpoint of these two values. Where a preservative composition contains two biocidal compounds at a particular ratio, the toxic index is the estimated minimum concentration of each biocide required for effective protection of the substrate from the target organism. In Figure 1 of the accompanying drawings, points A and B are the toxic index values for biocidal compounds Y and X respectively and the straight line between these two points illustrates the toxic index values which would be obtained if the biocidal effects of compounds X and Y are merely additive. If, for any particular ratio of X:Y, the toxic index value is found to be below the straight line (e.g. at point C), then compounds X and Y are synergistic at that particular ratio.

A convenient method of assessing the synergistic properties of a formulation is to use a 'synergistic index'. This may be defined as:

$$\text{Synergistic Index (SI)} = \frac{\text{Theoretical toxic index}}{\text{Actual toxic index}}$$

The theoretical toxic index may be calculated by interpolation to the theoretical line of action. A SI of 1 indicates no synergism. As the SI increases, so the degree of synergism also increases.

B: Wood Preservative Efficacy

Testing was carried out to determine the performance of active ingredients alone and in mixture using a soft rot soil burial method. The method used is similar to that described by the European pre-standard ENV-807 and challenges the treated wood in a wet soil environment to soft rot fungi belonging to the groups *Ascomycotina* and

Deuteromycotina.

Beech (*Fagus sylvatica*) blocks measuring 5 x 15 x 30 mm were prepared from local grown, seasoned, knot-free sapwood. After oven drying and weighing, the blocks were vacuum impregnated (in groups of 6 replicates) with retentions of the test preservatives which had been freshly prepared using deionised water as the diluent.

The following preservative combinations were tested:

Bethoxazin/Propiconazole (1:1)
Bethoxazin/Propiconazole/Tebuconazole (2:1:1)
Bethoxazin/Bardap 26 (1:5)
Bethoxazin/Bardap 26/Cyproconazole (2:10:1)

After treatment, the blocks were covered with polythene for a period of one week to reduce the drying rate and allow any fixation reactions to occur. They were then fully ventilated by standing on the laboratory bench for 2 weeks and allowed to dry.

Each series of blocks was then exposed in John Innes (No. 2) compost, previously wetted to 110% of water holding capacity using deionised water. The test systems were then incubated for 14 weeks at 28°C.

Following incubation, blocks were removed from the soil, gently rinsed in clean water and then oven dried and re-weighed.

Preservative retention and weight change data were calculated for each block and the results expressed as toxic limit values according to the criteria laid down in the test method EN113.

Results of Efficacy Testing

The results of the efficacy tests are given in the following table and expressed as toxic limit values in kgm^{-3} active ingredient retention.

Table 1

Results of Soil Testing with Organic Biocides	
Fungicide	Toxic Limit Value (kgm^{-3})
Tebuconazole	> 7.0
Propiconazole	> 7.0
Bethoxazin	> 0.77
Bethoxazin/Propiconazole	0.65-0.74
(1:1)	0.15-0.32
Bethoxazin/Propiconazole/ Tebuconazole (2:1:1)	0.54-1.11
Bethoxazin/Bardap 26 (1:5)	> 6.2
Bardap 26	0.58-1.18
Bardap 26/Bethoxazin/ Cyproconazole (10:2:1)	

A Toxic Limit Value of $>7.0kgm^{-3}$ indicates that at the concentrations tested, the highest of which was $7.0kgm^{-3}$, no effective protection of the wood was achieved.

Using the conventions of EN113, the following toxic limit values are expressed as individual active ingredients and mixtures. Therefore, taking tebuconazole as an example, the table below shows that the amount of tebuconazole required for effective preservation dropped from $>7kgm^{-3}$ when applied on its own to $0.08kgm^{-3}$ when it was part of a Bethoxazin/ Propiconazole/Tebuconazole mixture.

Table 2

Fungicide	Effective Retention of					
	Tebucona-zole	Cypro-conazole	Propi-conazole	Bethoxazin	Bardap 26	Mixture
Bethoxazin	-		-	>0.77	-	-
Tebuconazole	>7.0		-	-	-	-
Cyproconazole	-	1.25	-	-	-	-
Propiconazole	-		>7.0	-	-	-
Bethoxazin/ Propiconazole	-		0.345	0.345	-	0.69
Bethoxazin/Propiconazole/ Tebuconazole	0.8		0.08	0.16	-	0.32
Bethoxazin/Bardap 26	-		-	0.185	0.925	1.11
Bardap 26	-		-	-	>6.2	-
Bardap/Bethoxazin/ Cyproconazole	-	0.068	-	0.14	0.68	0.88

Where the lower toxic limit value provides a weight loss of 10% m/m or greater, then the upper toxic limit value has been used to indicate the probable effective retention of preservative; this is in accordance with EN113.

From this data, it can be seen that combinations of these organic biocides with Bethoxazin provide a significant enhancement in preserving ability towards microfungi that attack wood in contact with soil. The oxathiazine and the triazole/quaternary ammonium compound work synergistically to protect the wood substrate from fungal attack.

The results have been plotted in Figures 2, 3, 4 and 5 which show expected effect of combining the various biocides at the ratios tested with the actual results obtained for the combinations of biocides.

A further demonstration of synergism can be derived by

calculating a synergistic index value (SI) as described above. This compares the toxic threshold obtained in the test (Table 3) with the theoretical values which can be derived from Figures 2-5.

These results are provided in the following table.

Table 3

Formulation	Toxic threshold value (kgm^{-3} ai)	Theoretical value (kgm^{-3} ai)	Synergistic Index (SI)
Bethoxazin/ Propiconazole (1:1)	0.69	1.4	2.03
Bethoxazin/Propiconazole/ Tebuconazole (2:1:1)	0.32	1.4	4.37
Bethoxazin/Bardap 26 (1:5)	1.11	2.7	2.43
Bardop 26/Bethoxazin/ Cyproconazole	0.89	1.065	1.20

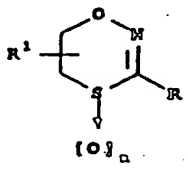
These values clearly show significant synergism at the ratios tested. In the case of the 3-way combination, some additional synergy is noted over and above that derived from either a combination of Bethoxazin plus azole or Bethoxazin plus Bardap 26.

CLAIMS

1. A preservative composition comprising, in synergistic proportions, an oxathiazine compound plus one or more of a quaternary ammonium compound and a triazole compound.

2. A composition as claimed in claim 1 which comprises an oxathiazine compound, a quaternary ammonium compound and a triazole compound.

3. A composition as claimed in claim 1 or claim 2 wherein the oxathiazine compound is a compound of formula (I)



(I)

wherein n is 0, 1 or 2; R^1 is hydrogen, C_1-C_4 linear or branched alkyl, or benzyl; and

R is:

(a) phenyl; naphthyl; phenyl substituted with 1 to 3 of the following substituents:

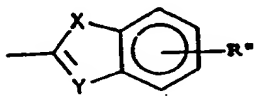
hydroxyl, halo, C_1-C_{12} alkyl, C_5-C_6 cycloalkyl, trihalomethyl, phenyl, C_1-C_5 alkoxy, C_1-C_5 alkylthio, tetrahydropyranyloxy, phenoxy, (C_1-C_4 alkyl)carbonyl, phenylcarbonyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, carboxy or its alkali metal salt, (C_1-C_4 alkoxy)carbonyl, (C_1-C_4 alkyl)aminocarbonyl, phenylaminocarbonyl, tolylaminocarbonyl, morpholinocarbonyl, amino, nitro, cyano, dioxolanyl, or (C_1-C_4 alkoxy)iminomethyl;

pyridinyl; thienyl, preferably when n is not 2; furanyl; or thienyl or furanyl substituted with 1 to 3 of the

following groups:

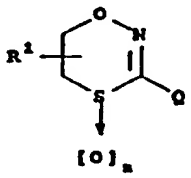
alkyl, alkoxy, alkylthio, alkoxycarbonyl, halogen, trihalomethyl, cyano, acetyl, benzoyl, nitro, formyl, alkoxyaminomethyl, phenyl, or phenylaminocarbonyl, wherein the alkyl or alkoxy moiety is C_1-C_4, linear or branched;

or

(b) 

wherein X is oxygen or sulfur; Y is nitrogen, -CH-, or -C(C_1-C_4 alkoxy)-; and R" is hydrogen or C_1-C_4 alkyl.

4. A composition as claimed in claim 3 wherein the oxathiazine compound is a compound of formula (II)

 (II)

wherein n is 0, 1 or 2, R^1 is hydrogen, C_1-C_4 linear or branched alkyl, or benzyl; and

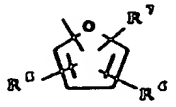
Q is:

(a)

wherein R^2, R^3 and R^4 are, individually, hydrogen, alkyl, alkoxy, alkylthio, alkoxycarbonyl, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, alkoxyaminomethyl, phenyl, or phenylaminocarbonyl,

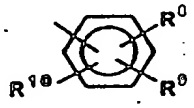
wherein the alkyl or alkoxy moieties are all C_1-C_4, linear or branched, with the proviso that at least one of R^2, R^3 or R^4 must be other than hydrogen;

(b)



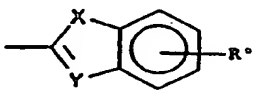
wherein R^5, R^6 and R^7 are, individually, hydrogen, C_1-C_4 alkoxy, C_1-C_4 alkylthio, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, phenyl, or phenylaminocarbonyl, with the proviso that at least one of R^5, R^6 or R^7 must be other than hydrogen;

(c)



wherein R^8, R^9 and R^{10} are, individually, hydroxyl, halo, C_1-C_{12} alkyl, C_5-C_6 cycloalkyl, trihalomethyl, phenyl, C_1-C_5 alkoxy, C_1-C_5 alkylthio, tetrahydropyranyloxy, phenoxy, (C_1-C_4 alkyl)carbonyl, phenylcarbonyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, carboxy or its alkali metal salt, (C_1-C_4 alkoxy)carbonyl, (C_1-C_4 alkyl)aminocarbonyl, phenylaminocarbonyl, tolylaminocarbonyl, morpholinocarbonyl, amino, nitro, cyano, dioxolanyl, or (C_1-C_4 alkoxy)iminomethyl; or

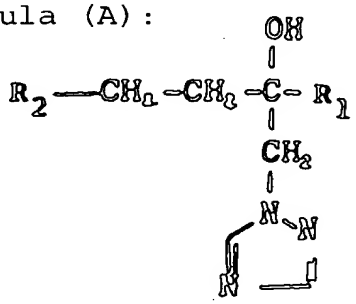
(d)



wherein X is oxygen or sulfur; Y is nitrogen, -CH-, or -C(C_1-C_4 alkoxy)-; and R" is hydrogen or C_1-C_4 alkyl.

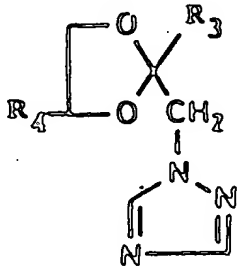
5. A composition as claimed in claim 4 wherein the oxathiazine compound is selected from 3-(benzo[b]thien-2-yl)-5,6-dihydro-1,4,2-oxathiazine 4-oxide and 5,6-dihydro-3-(2-thienyl)-1,4,2-oxathiazine, 4-oxide.

6. A composition as claimed in any one of the preceding claims wherein the triazole compound is selected from compounds of formula (A):



(A)

wherein R_1 represents a branched or straight chain C_{1-5} alkyl group and R_2 represents a phenyl group optionally substituted by one or more substituents selected from halogen atoms or C_{1-3} alkyl, C_{1-3} alkoxy, phenyl or nitro groups and compounds of formula (B):

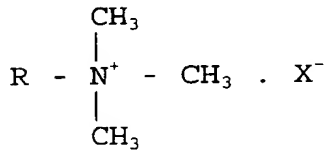


(B)

wherein R_3 is as defined for R_2 above and R_4 represents a hydrogen atom or a branched or straight chain C_{1-5} alkyl group.

7. A composition as claimed in claim 6 wherein the triazole compound is selected from the group comprising tebuconazole, propiconazole, azaconazole, hexaconazole, difenaconazole, cyproconazole, bromuconazole, epoxiconazole, metconazole, triticonazole, fenbuconazole, flusilazole, tetraconazole and penconazole.

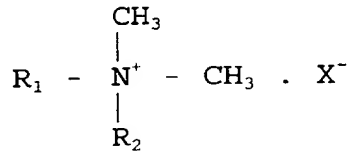
8. A composition as claimed in any one of the preceding claims wherein the quaternary ammonium compound is selected from compounds of formula (III):



(III)

wherein R is an alkyl group having between 6 and 18 carbon atoms and X^- is an anion which allows ready water solubility of the quaternary ammonium salt,

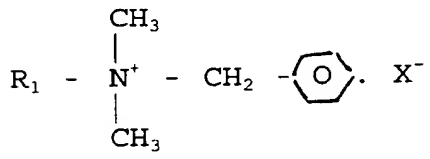
compounds of formula (IV):



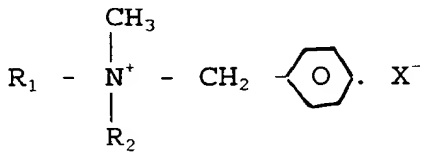
(IV)

wherein R_1 and R_2 are alkyl groups which may be the same or different and which contain between 6 and 18 carbon atoms, and X^- is an anion as described above,

compounds of formulae (V) or (VI):



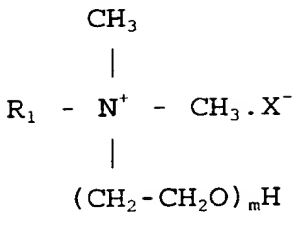
(V)



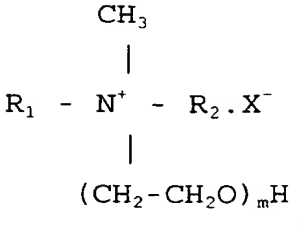
(VI)

wherein R_1 and R_2 are alkyl groups which can be the same or different and which contain between 6 and 18 carbon atoms and X^- is an anion as described above,

compounds of formulae (VII) or (VIII):



(VII)



(VIII)

wherein R_1 and R_2 are alkyl groups which may be the same or different and which contain between 6 and 18 carbon atoms and wherein m is a number between 1 and 20.

9. A method of treating a substrate of wood or other material which comprises applying to the substrate a composition as claimed in any one of the preceding claims.

10. A method as claimed in claim 9 wherein the substrate is affected by or at risk of being affected by soft rot.

11. A method as claimed in claim 9 or claim 10 wherein the substrate is affected by or at risk of being affected by *Ascomycotina* or *Deuteromycotina*.

12. A method of preserving wood or other material which comprises applying to the wood or other material a composition as claimed in any one of claims 1 to 8.

13. Use of a quaternary ammonium compound or a triazole to enhance the activity of an oxathiazine against *Ascomycotina* and *Deuteromycotina*.

FIG. 1

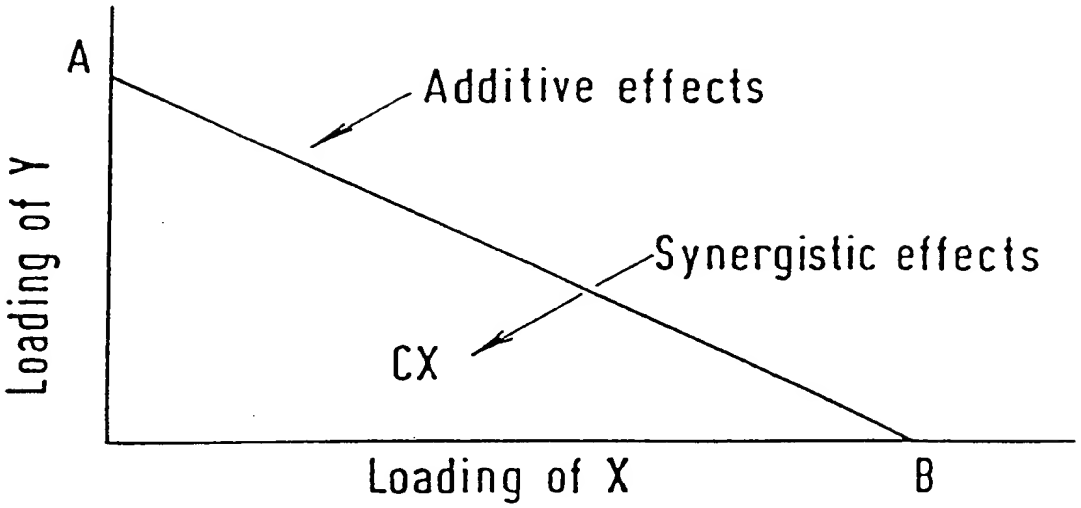

A
Additive effects
Loading of Y
Synergistic effects
CX
Loading of X
B

Figure 2

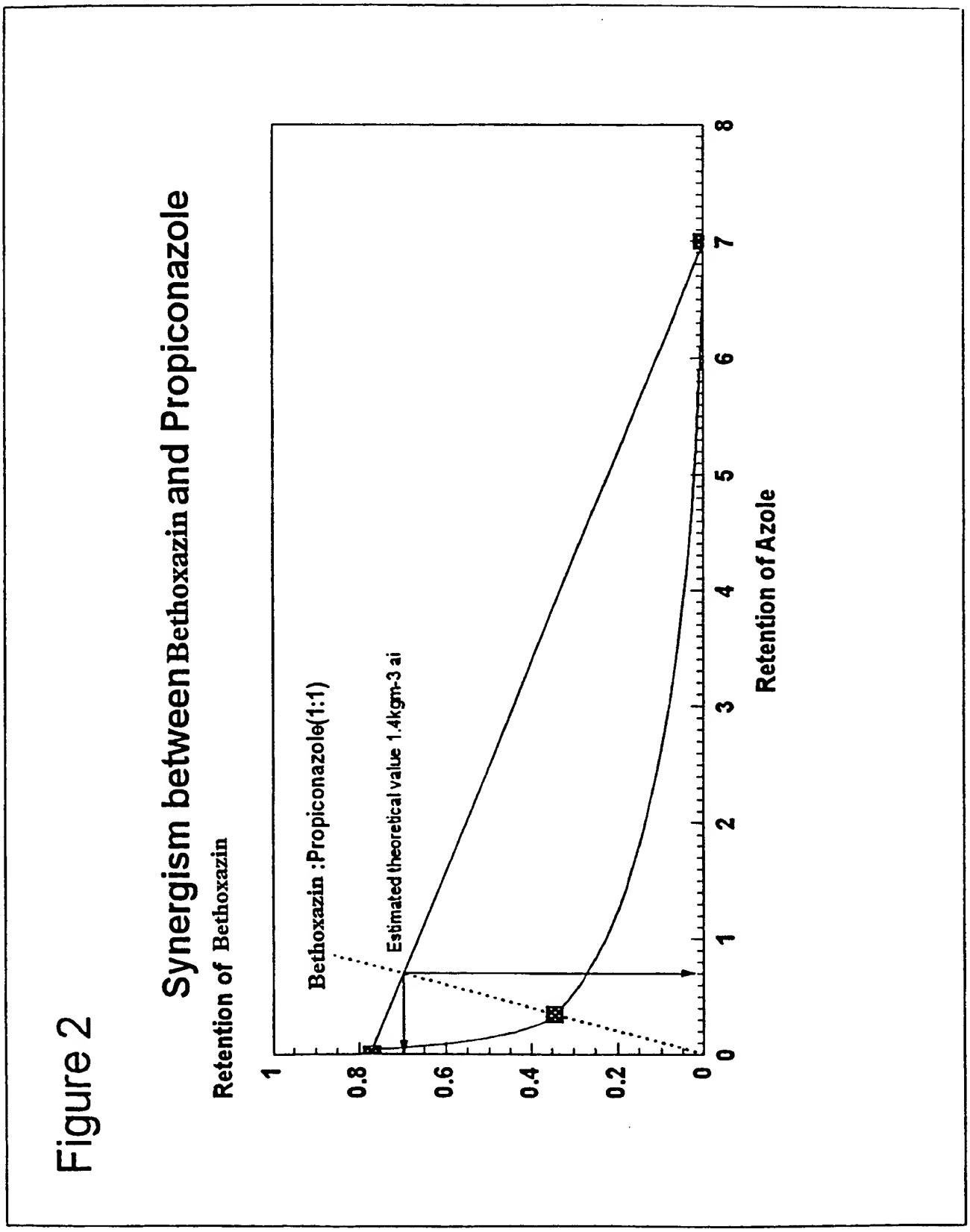

Synergism between Bethoxazin and Propiconazole
Retention of Bethoxazin
Retention of Azole
Bethoxazin :Propiconazole(1:1)
Estimated theoretical value 1.4kgm-3 ai
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8

Figure 3

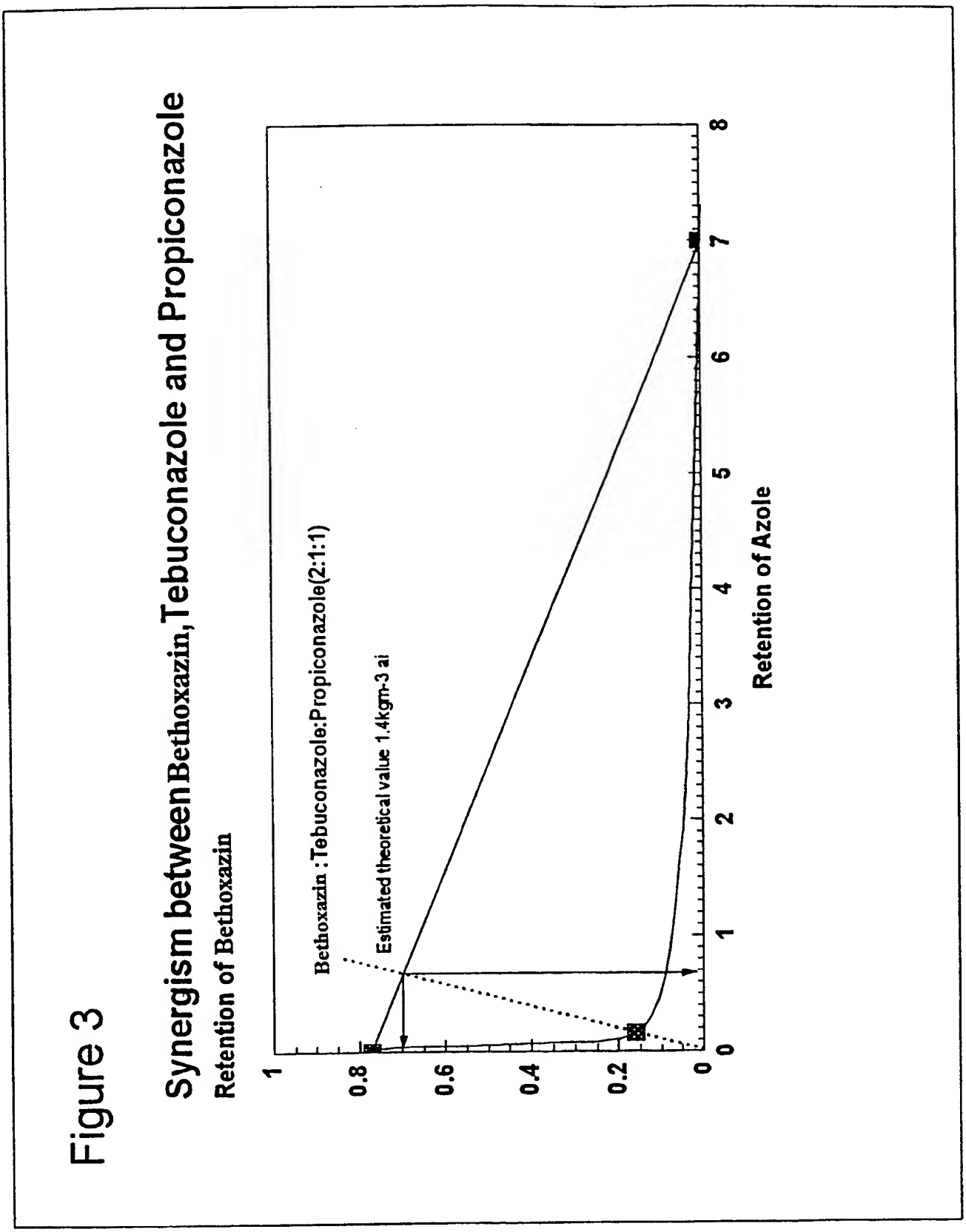

Synergism between Bethoxazin, Tebuconazole and Propiconazole
Retention of Bethoxazin
Bethoxazin : Tebuconazole:Propiconazole(2:1:1)
Estimated theoretical value 1.4kgm-3 ai
Retention of Azole
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8

Figure 4

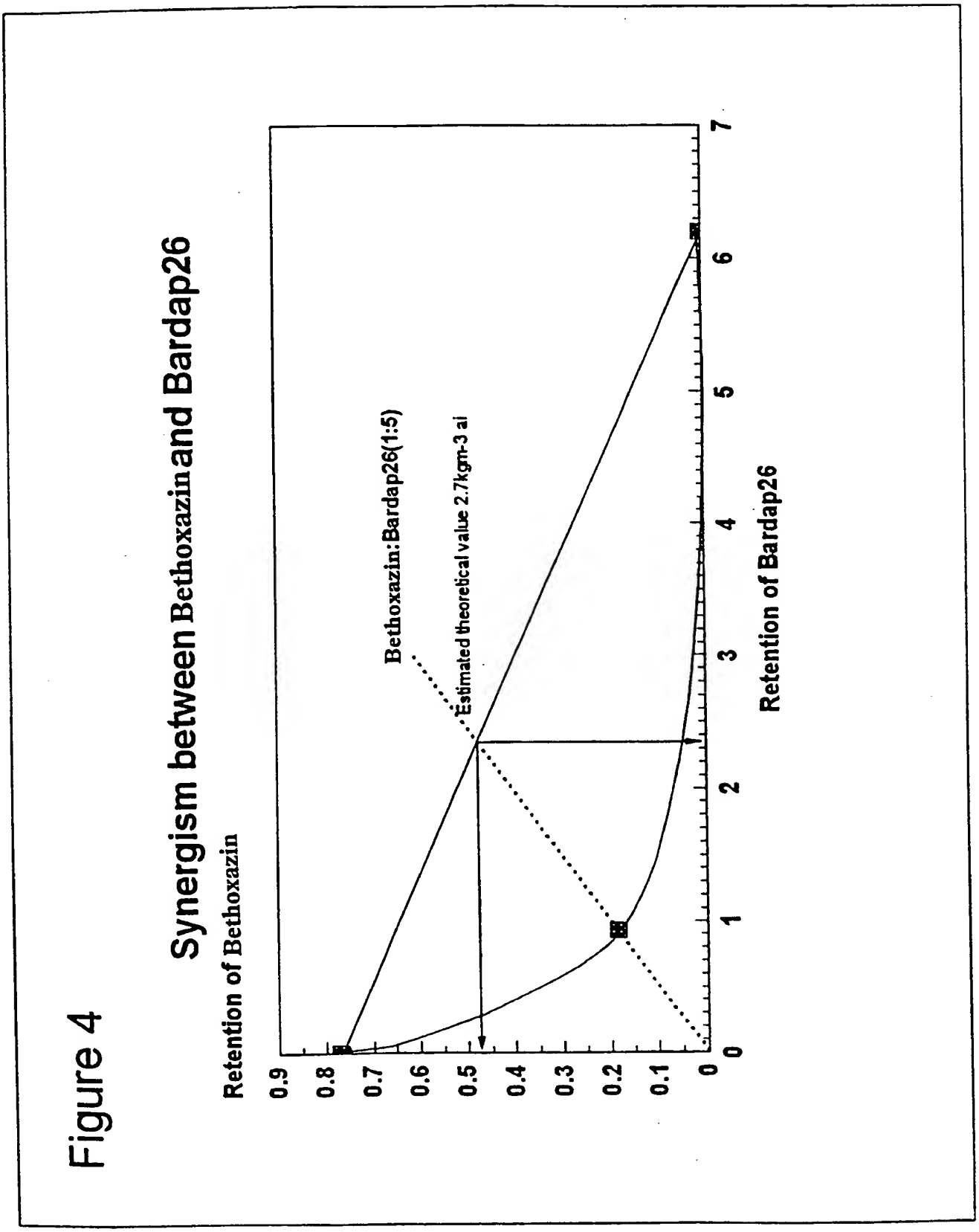
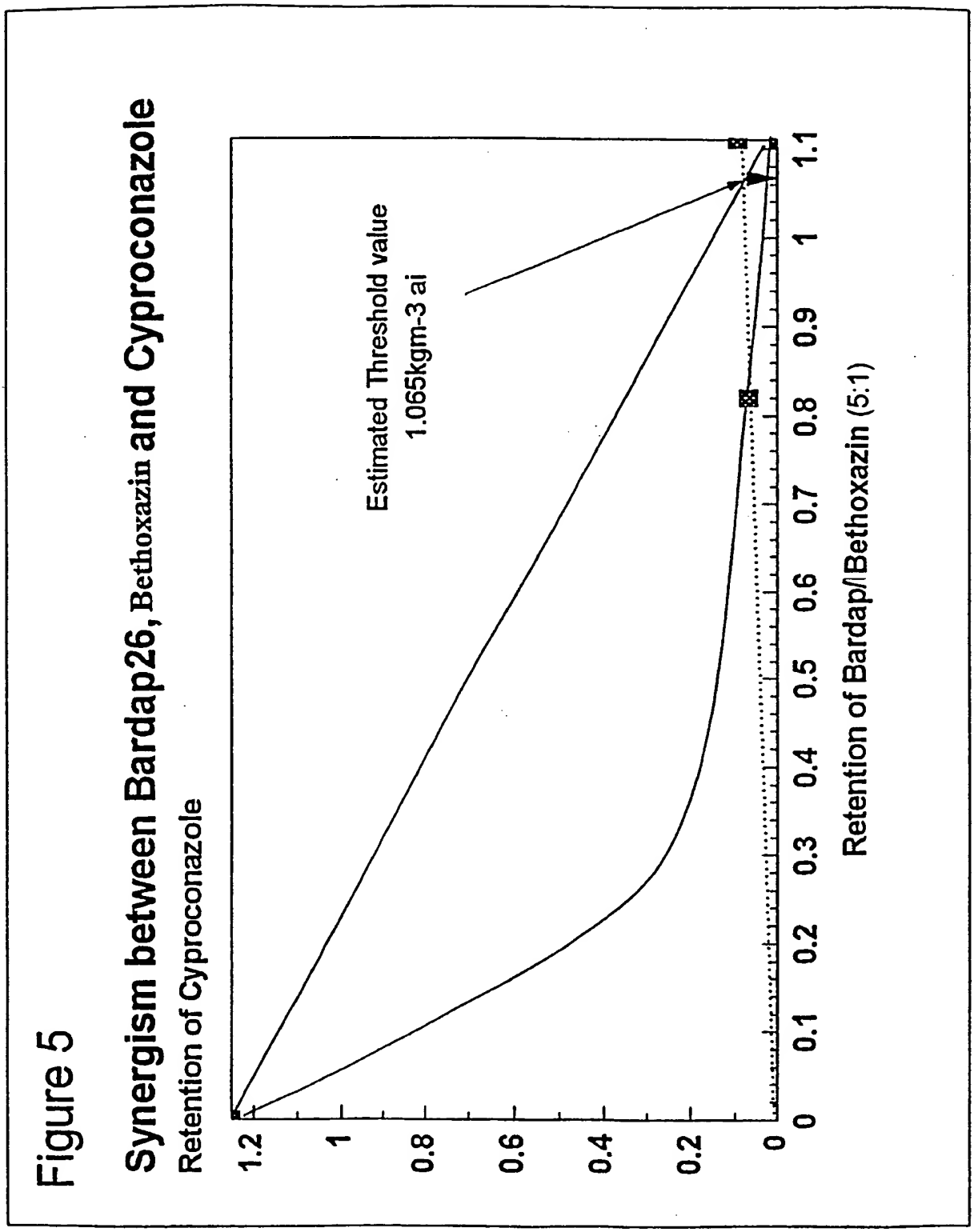

Synergism between Bethoxazin and Bardap26
Retention of Bethoxazin
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
7
Retention of Bardap26
Bethoxazin:Bardap26(1:5)
Estimated theoretical value 2.7kgm-3 ai

Figure 5


Synergism between Bardap26, Bethoxazin and Cyproconazole
Retention of Cyproconazole
Estimated Threshold value
1.065kgm-3 ai
1.2
1
0.8
0.6
0.4
0.2
0
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1 1.1
Retention of Bardap/Bethoxazin (5:1)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/03997

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B27K3/50 A01N43/88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N B27K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 06043 A (UNIROYAL CHEM CO INC ;UNIROYAL CHEMICAL LTD (CA)) 2 March 1995 (1995-03-02) page 12, line 1-17; claim 4	1
A	EP 0 104 940 A (UNIROYAL INC ;UNIROYAL LTD (CA)) 4 April 1984 (1984-04-04)	
A	WO 95 05739 A (JANSSEN PHARMACEUTICA NV ;GESTEL JOZEF FRANS ELISABETHA (BE)) 2 March 1995 (1995-03-02)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 February 2000	09/03/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Dalkafouki, A

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